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Research Article

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Removal of malachite green, a hazardous dye using graphene oxide as an adsorbent from aqueous phase

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ABSTRACT

Adsorptive potential of an agricultural waste, oat hull for the removal of a dye, Malachite Green from aqueous solutions was investigated. Graphene oxide was used as efficient adsorbent for the rapid removal of Malachite Green from the aqueous phase, the whole adsorption process was well investigated and elucidated. The impact of several influential parameters such as contact time, initial dye concentrations, initial solution pH and temperature was well studied and optimized. The optimized time for adsorption process was 100 min. The maximum removal efficiency occurred at optimized pH 3 of aqueous solutions. Increasing the initial concentration of Malachite Green dye adsorption capacity was decreased, this may be due to repulsion between Malachite Green negative charge and the graphene oxide surface negative charge. The effect of temperature revealed that adsorption process of dye on the developed adsorbent was endothermic. The adsorption equilibrium data of Malachite Green dye on to the GO adsorbent surface were found to be well fitted and in good agreement with the type (I) Langmuir isotherm; because it possesses high value of linear regression (R^2 = 0.999) and least value for chi-square statistic (X^2 = 2.28).

Keywords: Adsorption; Mass Transfer; Isotherm; Malachite Green

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INTRODUCTION

Now a day the major concern of the environmentalist is presence of toxic dye in effluents because it possesses adverse effects on many forms of life. The evacuation of colors and dye in the nature is a matter of concern for both esthetical and toxicological reasons [1]. Some of the Chemical industries produced dye wastewaters and are the

main contributors of colored effluents such as printing, dyeing, textile, food, cosmetics coloring, papermaking, and paper [2–6]. There are more than 105 commercially available dyes with over $7 * 10^5$ tons of dye produced annually [7]. Several treatment techniques and methods like flocculation, ozonation, membrane filtration, ion exchange, coagulation/flocculation, oxidation, electrochemical or photochemical method, degradation by biological and adsorption have been employed to refine and purify the wastewater from these non-biodegradable noxious dye [8–11]. Adsorption at solution phase today widely used as useful way to sequester and remove the organic dyestuffs from the water because of its easy operation, low cost and high efficiency [9]. Several other previously developed adsorbents such as carbon nanotubes [12–19], MWCNTs (multi-walled carbon nanotubes) [20, 21], nanoparticles and nanocomposites [22–26], rubber tire [27, 28], and other low cost adsorbents [29–34] etc. are extensively used for the rapid removal of noxious impurities from the aqueous solution. Some adsorbents such as activated carbon, zeolites, biomaterials, nanoparticles, polymers, etc., have been extensively used for the fast adsorption of noxious dye, but the adsorption efficiency of such adsorbents has been reported to be very low. Therefore, a keen attention and serious effort of different research groups is required to search for the more efficient adsorbents. To solve these defects of traditional sorbents, graphite oxide sheet or called graphene oxide (GO), a two dimensional nonmaterial prepared from the chemical oxidation of natural graphite [35] have been extensively investigated over a decade for its application in the field of wastewater treatment. For the production of GO the oxidation process on the graphite sheet was carried out to introduce the abundant oxygen-containing functional groups such as carbonyl, epoxy, carboxyl and hydroxyl on the GO surfaces [36]. Large specific surface area and these groups make GO a superb platform for loading grafting b-CD and magnetic nanoparticles [37]. Graphene oxide easily provide platform for the liquid–solid separation because of its integrated magnetic properties [38].

The aim of the present study was to synthesize an efficient adsorbent in order to do this, an efficient nonmaterial graphene oxide (GO) was synthesized and characterized using various analytical techniques and the developed nanoparticle was accomplished and exploited as adsorbent for rapid removal of Malachite Green dye from the aqueous solution.

EXPERIMENTAL SECTION

The single layer graphene oxide with the specifications: aqueous dispersion: 175 ml, concentration: 500 mg/L, composition: carbon (79%), oxygen (20%), flake size: 0.3–0.7 lm, thickness: 1 atomic layer – at least 80% and color: brown was used at all adsorption experiments as adsorbent, specific surface area was determined 133 m2/g prepared from Graphene Supermarket, USA.

Malachite Green (MG) used in this study was procured from E. Merck (Mumbai, India) having 99.0% purity was used for the preparation of dye solution without any prior purification. Dye stock solution (1000 mg L−1) was prepared by dissolving 1.0 g of MG in 1000 mL of double distilled water. The dye solutions of different concentrations (25–200 mg/L) were prepared by diluting the stock solution with suitable volume of double distilled water. Malachite Green was indicated in Fig. 1.

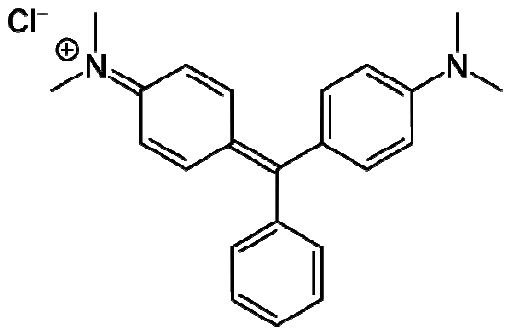


Fig. 1: Malachite Green

Adsorption study:

To perform the adsorption experiments samples were prepared by adding the 20 mg of GO as adsorbent in to 20 mL dye solutions with concentrations 25 mg $_{L^{-1}}$, for batch adsorption experiments.

The concentrations of dye in the aqueous solutions were collected and determined using the UV–Vis spectrophotometer furnished by Varian (Cary 100 Bio) (London–England) after a certain period of time at 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 min. Adsorptions time curve for removal of MG dye by GO as adsorbent is shown in Fig. 2.

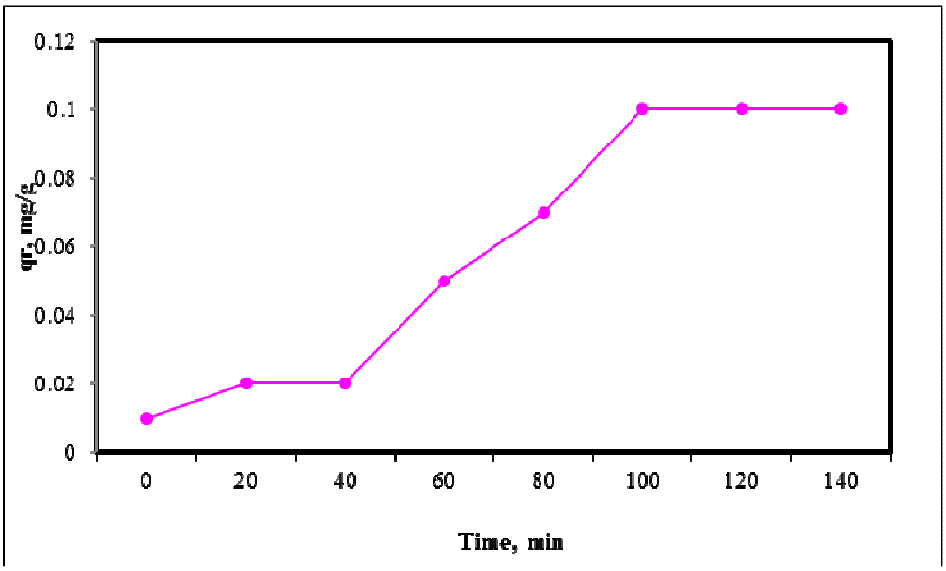


Fig. 2: Effect of contact time on the removal of Malachite Green dye on GO adsorbent, initial concentration: 0.2 mg/L; adsorbent dosage: 20 mg and T: 298 K, pH: 3

By doing the preliminary experiments 100 min was confirmed as best contact time of adsorption Malachite Green dye on GO surface. Because 100 min was sufficient to attain equilibrium between GO surface and the dye so this time was used as optimized contact time. The whole solute–solvent was placed on ultrasonic bath which was maintained at the fixed temperature range 30–40 ^{0} C; hence the adsorption experiment was carried out at fixed temperature. Ultrasonic bath (71020 DTH-E; Model 1510 DTH, 220 V; EMS Company) was used to prevent the aggregation of particles and forming bulk, it helps in the proper mixing of solvent containing impurities and adsorbent.

The samples including dye and adsorbents were filtered by a 0.2 µm cellulose membrane. Then the suspensions containing the dye and adsorbent were centrifuged for 4 min at 4500 rpm, which was later followed by the measurement of the remaining concentrations Malachite Green dye using UV–Vis spectrophotometer. Then for equilibrium study i.e. the amount of Malachite Green dye removed by the GO were determined by the difference between the initial and residual concentration of dye solution. The adsorption capacity of Malachite Green dye on graphene oxide was calculated using the Eq. (1) [39, 40]:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

Where q_e is the amount of dye taken up by the adsorbent (mg $_g^{-1}$), C_0 was the initial dye concentration (mg $_L^{-1}$), C_e was the dye concentration after the adsorption process (mg $_L^{-1}$), m is adsorbent mass (g) and V is the volume of the dye solution (L) [41].

RESULTS AND DISCUSSION

Characterizations of GO

The surface textural and morphological properties of the developed adsorbent were carried out using Scanning electron microscopy and the obtained structure was presented in Fig. 3, it clearly revealed that the microstructures are present on the surfaces of graphene oxide.

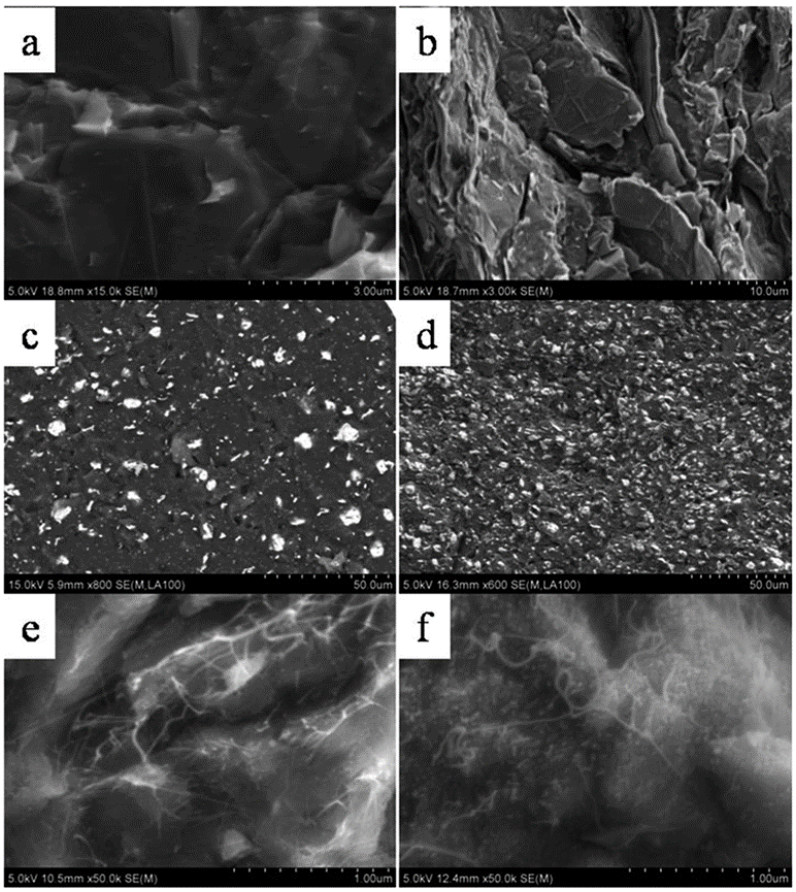


Fig. 3: SEM image of single layer graphene oxide surface prepared from Graphene Supermarket (a, c, e), USA and Graphene Oxide (b, d, f)

The FTIR pattern of graphene has a characteristic peak at 1610 $_{cm^{-1}}$ due to the aromatic C-C skeletal vibrations as shown in Fig. 4. The FTIR pattern of GO, which is shown in Fig. 4, reveals the presence of oxygen-containing functional groups. The peaks at 1226, 1398, and 1645.17, correspond to C-O-C stretching vibrations, C-OH stretching, and C-C stretching mode of the sp2 carbon skeletal network, respectively, while peaks located at 3143.7 and 3427.27 correspond to C-O stretching vibrations of the COOH groups and O-H stretching vibration, respectively. For carrying out the adsorption studies of adsorbate–adsorbent system the temperate in the range of 30–50 ^{0}C and for this range the GO is almost constant and this adsorbent is stable. So, GO was not decomposed in this particular fixed range of temperature. Surface charge for GO was investigated and the researcher indicated that GO have negative surface charge, because have carboxylate group on surface graphene.

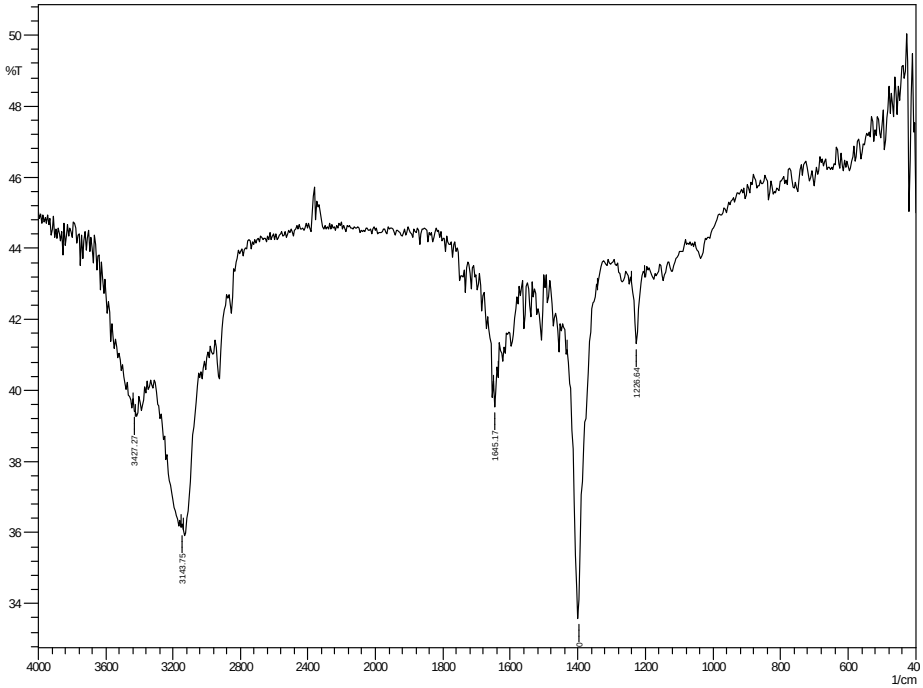


Fig. 4: Fourier transform infrared spectrum (FT-IR) for graphene oxide

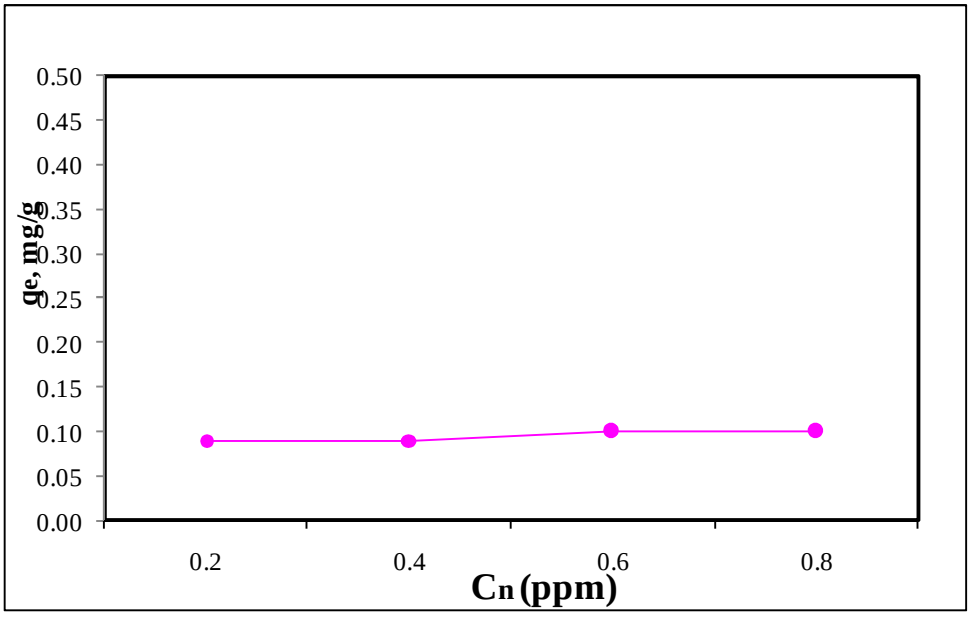
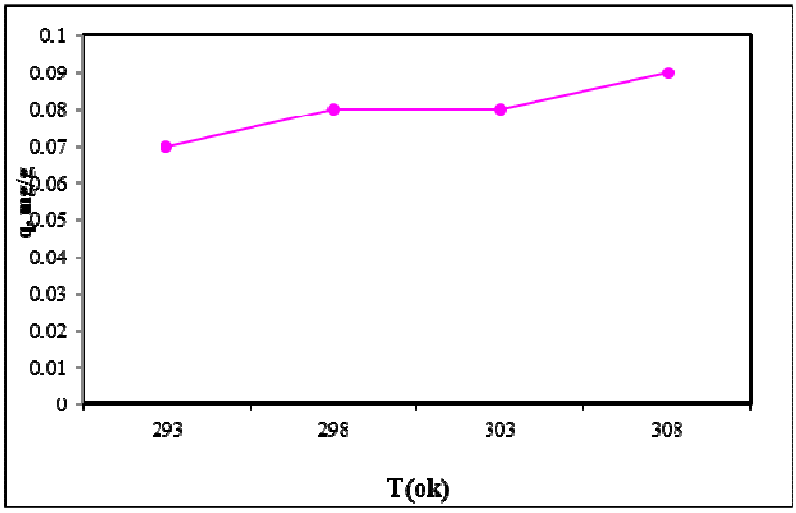


Fig. 5: Effect of initial concentration of Malachite Green dye on the removal by GO surface, initial concentration: 0.2, 0.4, 0.6 and 0.8 mg/L; adsorbent dosage: 20 mg and T: 298 K, pH: 3



. Fig. 6: Effect of temperature on the adsorption of Malachite Green dye by GO adsorbent, initial concentration: 0.2 mg/L; adsorbent dosage: 20 mg and T: 293, 298, 303 and 308 K, pH: 3.

Effect of initial concentration

Effect of initial concentration of dye on adsorption capacity was well studied and elucidated. For determining the effect of initial concentration of MG dye in solution, the adsorption experiments were performed in several initial concentrations varying from 0.2 to 0.8 mg L_1 at 298 K and optimized pH 3 for 100 min. As it can be clearly indicted in Fig. 5, On the other hand, increasing the initial concentration of Malachite Green dye the adsorption capacity was decreased; this may be due to repulsion between Malachite Green negative charge (Fig. 1 and the graphene oxide surface negative charge. The obtained facts can be well established by considering the chemical structure for Malachite Green; MG possesses negative charge. So, the electrostatic forces between MG with GO was repulsive in nature .So, it revealed the increased adsorption and reduced adsorption for MO, respectively.

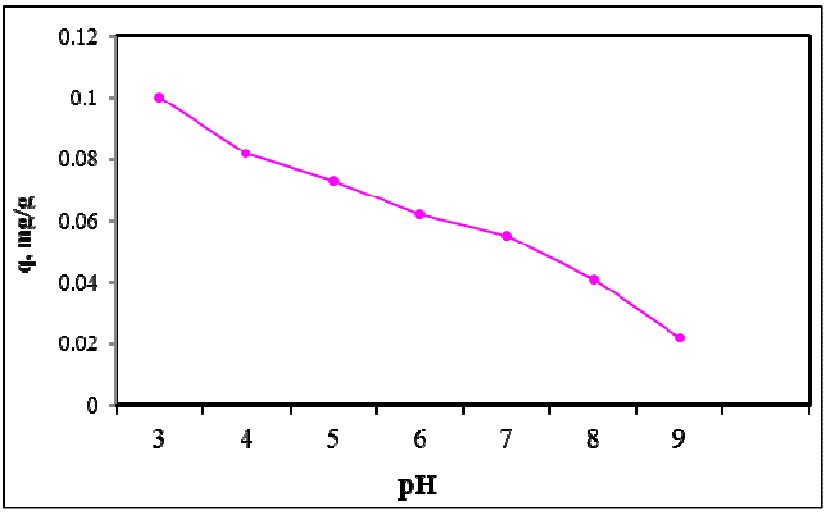


Fig. 7: Effect of pH on the Malachite Green dye removal by GO adsorbent, initial concentration: 0.2 mg/L; adsorbent dosage: 20 mg and T: 298 K

Effect of temperature on the adsorption process:

To determine the effect of temperature on adsorption of Malachite Green dye from solution phase by graphene oxide adsorbent, the experiments were carried out at different temperature from 293 to 308 K at 100 min and pH 3. The curve of effect of temperature on the dye adsorption capacity on GO surface at temperature ranging from 283 to 308

K is displayed in Fig. 6. As shown in Fig. 6 with increasing the temperature removal of Malachite Green dye by graphene oxide adsorbent was increased. It revealed towards the endothermic nature of the process.

Effect of pH:
To determine the effect of initial solution pH on removal of Malachite Green dye by GO, the adsorption experiments were performed at several pH from 3 to 9, at temperature 298 K and contact time 100 min. For all adsorption experiments observed that with increasing pH value from 3 to 9, the removal of dye by graphene oxide surface was decreased as shown in Fig. 7. The high removal capacity of dye by graphene oxide surface at low pH values may be explained due to electrostatic attraction occurred between GO surface and Malachite Green dye. In addition from Fig. 7, it can be seen that adsorption percentage of Malachite Green dye is decreasing. [42].

Adsorption isotherm study:
Effect of initial concentration of dye on removal by GO adsorbent is shown in Fig. 5. With increasing the initial concentration of Malachite Green dye from 0.2 to 0.8 ppm adsorption capacity of Malachite Green dye was decreased. The models analyze base interaction between solute molecules on solution (liquid phase) and adsorbents surface (solid phase). So, we can use many models such as kinetics or isotherm model. Many models are using on adsorption process, but some models such as Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Halsey and others are easily used and more valid between experiment and theoretical date. Also, many parameters can be calculated from these isotherms.

In this study, for the adsorption capacity of basic red 12 and Malachite Green dye by GO adsorbent, simulated by the Temkin [43], the Freundlich [44], and the Langmuir [45,46].

Also, the models were evaluated by the adjusted determination factor (R^2adj); in addition, to estimate the fitness of isotherm equations to the experimental data, the chi-square statistic (X^2) was used to measure the isotherm constants [47].

Temkin isotherm model:
The effects of some indirect adsorbent–adsorbate interaction on adsorption isotherms considered Temkin and suggested that the heat of adsorption of all the molecules in the layer would linearly decrease with coverage [43]. The Temkin isotherm has been applied in the following form:

$$qe = B \ln A + B \ln C_e \quad (3)$$

Where A (l/mg) is the Temkin parameter related to the equilibrium binding energy and B is the Temkin constant related to adsorption heat. The Temkin constants can be derived from the plot of qe versus ln Ce. The obtained results are presented in Table 3 and the curves are shown in Fig. 8.

Freundlich isotherm model:
The Freundlich [44] isotherm is derived by assuming a heterogeneous surface with a no uniform distribution of the heat of sorption over the surface. It can be linearly expressed as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

Where n and KF are adsorption intensity and the Freundlich parameters related to adsorption capacity, respectively. If the value of 1/n is lower than 1, it indicates a normal adsorption; otherwise, it is indicative of cooperative adsorption. The Freundlich constants can be obtained from the plot of log qe versus log Ce [25]. The obtained results are presented in Table 3 and the curves are shown in Fig. 9.

Table 3: Adsorption Isotherm Parameters

Langmuir			FREUNDLICH			Temkin		
Ka(L/mg)	Qm(mg/g)	R2	n	Kf(mg/g)	R2	Kt(L/mg)	B	R2
0.12813370	54.347826	0.996	2.99043	101.142	0.9775	e0.475952575	11.049	0.9999

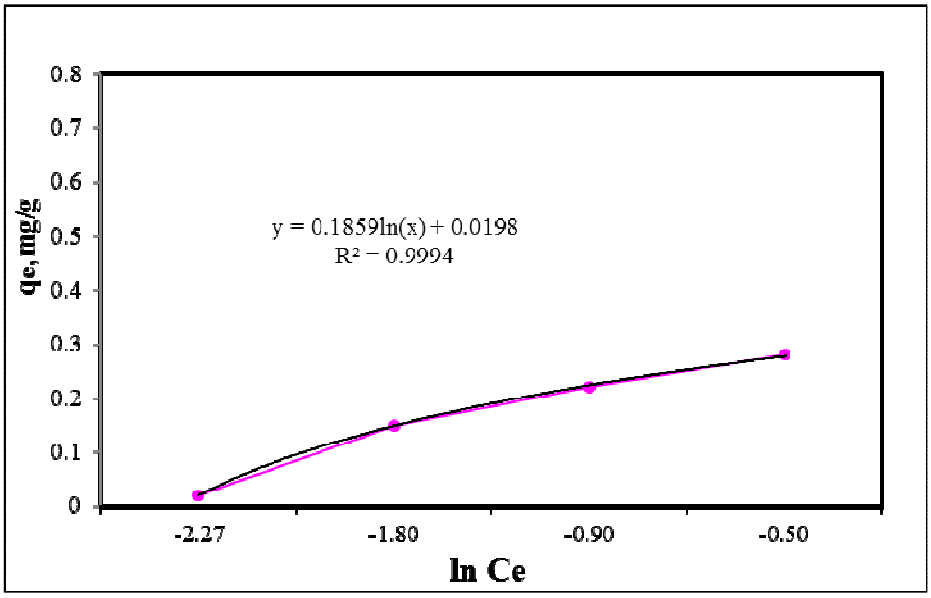


Fig. 8: Temkin adsorption isotherm of and Malachite Green dye on GO surface, conditions: dye initial concentration: 0.2, 0.4, 0.6 and 0.8 mg/L; adsorbent dosage: 20 mg; time: 100 min; T: 298 K and pH 3

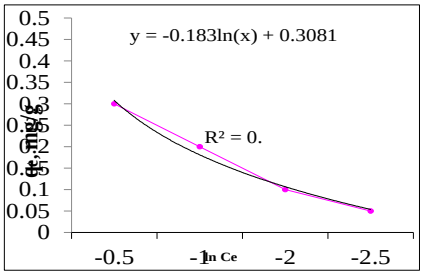


Fig. 9: Freundlich adsorption isotherm of basic Malachite Green dye on GO surface, conditions: dye initial concentration: 0.2, 0.4, 0.6 and 0.8 mg/L; adsorbent dosage: 20 mg; time: 100 min; T: 298 K and pH 3

Langmuir isotherm model:

One of the most prevalent isotherm models which are widely used in the equilibrium study is the Langmuir isotherm model. In this study four types of the linearized Langmuir isotherm were used which can be expressed as [45]:

$$\frac{C_e}{q_e} = \frac{K_L C_e}{1 + K_L C_e}$$

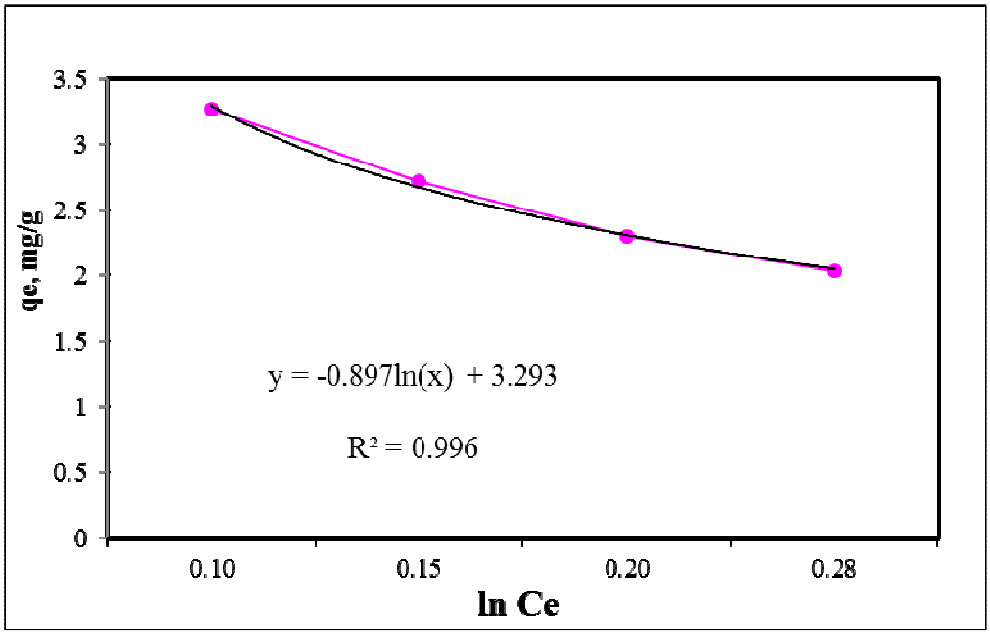


Fig. 10: Type 1 of Langmuir isotherm for adsorption of Malachite Green dye on GO surface, conditions: dye initial concentration: 0.2, 0.4, 0.6 and 0.8 mg/L; adsorbent dosage: 20 mg; time: 100 min; T: 298 K and pH 3

CONCLUSION

In summary, the adsorption capacity of MO dye on GO surface from aqueous solutions was well investigated and elucidated. The optimized values of initial concentration of dye, contact time, pH and adsorbent dose were found to be 0.2 mg/L, 100 min, 3 and 20 mg, respectively. The effect of temperature revealed that the adsorption process of dye on adsorbents was endothermic. The obtained adsorption equilibrium data for the experiments was carried out using four types of the Langmuir, Freundlich, Temkin isotherm models. Results clearly depict that adsorption of MG dye on to the GO adsorbent surface was well fitted and found to be in good agreement with the Langmuir isotherm, the obtained regression constant value (R^2) was found to be 0.999 and low value the chi-square statistic (X^2).

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